

BEST AVAILABLE COPY

PATENT SPECIFICATION

NO DRAWINGS

1,103,212

1,103,212



Date of Application and filing Complete Specification: Feb. 26, 1965.

No. 8462/65.

Application made in United States of America (No. 347683) on Feb. 27, 1964.

Complete Specification Published: Feb. 14, 1968.

© Crown Copyright 1968.

Index at acceptance:—C3 P(4A, 4C10, 4C12X, 4C13B, 4C13C, 4C18, 4C20A, 4D3B1, 4D3B3, 4K10, 4S2, 5A, 5C13B, 5C13C, 5D2A, 5S2, 6A, 6C13B, 6C13C, 6D1, 6S2, 7A, 7C3, 7C11, 7C13B, 7C13C, 7D2A1, 7D2A2B, 7D2A3, 7S2, 8A, 8C13B, 8C13C, 8D1A, 8D1B, 8D2A, 8D2B2, 8D3A, 8D3B, 8D4, 8S2, 9A, 9C13B, 9C13C, 9D1B1, 9S2, 10A, 10C10, 10C12X, 10C13B, 10C13C, 10C18, 10C20A, 10K4, 10S2, 11A, 11C13B, 11C13C, 11D2A, 11S2); B5 N(17X, 17Y, 22X, 22Y, 67X, 68X, 78Y, 177, 178, 180, 188, 251, 254Y, 255Y, 256, 257, 258Y, 259, 261Y, 262Y, 263Y, 265Y, 266Y, 269Y, 270Y, 271Y, 272Y, 273Y, 274Y, 290Y, 295Y, 297Y, 570, 621, 624, 627, 629, 655, 663, 666, 670, 671, 674, 679, 750, 807)

Int. Cl.:—C 08 f 29/12

COMPLETE SPECIFICATION

Vinyl Polymer Overlay Films and Compositions for Forming the same

We, UNION CARBIDE CORPORATION, a corporation organised under the laws of the State of New York, United States of America, of 270, Park Avenue, New York, State of New

5 York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to thermoplastic vinyl polymer film forming compositions and films made from such compositions. More particularly the present invention relates 15 to vinyl polymer film forming compositions which films are characterized by a rough surface and which can be easily laminated to hard, smooth, impermeable substrates without air entrapment and which can be finished 20 to an optically smooth surface and methods for performing same.

It has long been known in the art that such identification devices as badges, cards, papers and the like could be surfaced with 25 plastic film or laminated between two plastic films. The plastic overlay or laminate in such instances provides the device with two particularly outstanding characteristics. First it protects the printed substrate, usually paper, from damage in use and secondly it makes alteration or tampering much more difficult. In more recent times the use of plastic based 30 identification-charge account plates has made it desirable to laminate a protective film over

at least the face of the plate to provide protection to printed material on the card and provide a hard long wearing printing surface for the plate indent. While the overlay or lamination of plastic film to air permeable substrates, such as paper, was accomplished with relatively few difficulties, the lamination of overlay films to hard smooth air impermeable substrates such as plastic sheet was not. It was found that during the lamination of the smooth films, air frequently became entrapped, causing unsightly blisters which makes the card unacceptable in appearance. This proclivity of the film toward air entrapment necessitates the rejection of many of the laminated products thereby reducing the efficiency of the process.

According to the present invention there is provided a thermoplastic composition capable of being extruded as a self-supporting film comprising a low melting thermoplastic vinyl polymer matrix resin as hereinafter defined and dispersed therein from 1 to 10 per cent by weight of the matrix resin of a particulate high melting vinyl polymer resin having an average particle size of from 20 to 120 microns in diameter, the fluxing temperature of said dispersed particulate resin being at least 20° C. higher than the fluxing temperature of said matrix resin.

By the term "low melting thermoplastic vinyl polymer resin" is meant those thermoplastic vinyl polymer resins which have a relatively low temperature fluxing range.

35

40

45

50

55

60

65

- While this range will vary from polymer to polymer these ranges are known to the art and are readily ascertained. For example the fluxing temperature ranges for matrix resin polyvinyl chloride is from about 165° C. to about 185° C.
- By the term "vinyl polymer matrix resins" as used herein is meant those resins prepared
- from the monomers containing the $-C=C-$ group, which contain groups exhibiting a dipole moment, and mixtures thereof which can be homopolymerized or copolymerized to form thermoplastic polymers and which can be utilized in accordance with the present invention. Illustrative of the vinyl monomers are the follows: vinyl aryls such as styrene, *o*-methoxystyrene, *p*-methoxystyrene, *m*-methoxystyrene, *o*-nitrostyrene, *m*-nitrostyrene, *o*-methylstyrene, *p*-methylstyrene, *m*-methylstyrene, *p*-phenylstyrene, *o*-phenylstyrene, *m*-phenylstyrene, vinylnaphthalene and the like; vinyl and vinylidene halides such as vinyl chloride, vinylidene chloride, vinylidene bromide and the like; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl chloroacetate, vinyl chloropropionate, vinyl benzoate, vinyl chlorobenzoate and the like; acrylic and *alpha*-alkyl acrylic acids, their alkyl esters, their amides and their nitriles such as acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, *n*-octyl acrylate, 2-ethylhexyl acrylate, *n*-decyl acrylate, methyl methacrylate, butyl methacrylate, methyl ethacrylate, ethyl ethacrylate, acrylamide, N-methyl acrylamide, N,N-dimethacrylamide, methacrylamide, N-methyl methacrylamide, N,N-dimethyl methacrylamide, acrylonitrile, methacrylonitrile, ethacrylonitrile, and the like; alkyl esters of maleic and fumaric acid such as dimethyl maleate, diethyl maleate and the like; vinyl alkyl ethers and ketones such as vinyl methyl ether, vinyl ethyl ether, vinyl isobutyl ether, 2-chloroethyl vinyl ether, methyl vinyl ketone, ethyl vinyl ketone, isobutyl vinyl ketone and the like; also vinyl pyridine, N-vinyl carbazole, N-vinyl pyrrolidine, ethyl methylene malonate and the like, and modified vinyl polymers such as polystyrene modified with rubber, polystyrene modified with hydrocarbon wax and the like.
- Groups which exhibit a dipole moment are generally referred to as polar substituents and include substituents such as ester, halogens, phenyls, ethers and the like.
- The vinyl polymer matrix resin should be of sufficiently high molecular weight to be extrudable as a continuous, self supporting film. While this minimum molecular weight varies from polymer to polymer, for a specific vinyl polymer such minimum values are well known in the art. For example, utilizing inherent viscosity as a measure of molecular weight, a vinyl chloride polymer matrix resin should exhibit an equivalent inherent viscosity of at least about .58 as determined by ASTM D-1243 Method A measured for 0.2 gram in 100 milliliters of cyclohexanone at 30° C. 70
- The maximum molecular weight of the matrix resin is limited only by processing factors such as extrudability. The matrix vinyl polymer resin should have a lower molecular weight than the vinyl polymer particulate dispersible resin used. Preferably the matrix resin should have an equivalent inherent viscosity of at least 0.1 less than the inherent viscosity of the particulate dispersible resin as measured by ASTM D-1243 Method A (0.2 gram in 100 milliliters at 30° C.). 75
- The particulate dispersed vinyl polymer resin can be any of the types of polymeric material illustrated above for the matrix resin. In fact it has been found highly desirable to utilize the same type of particulate resin as is used as the matrix resin as the refractive properties can be more easily matched, if optical clarity is desired. However this is not necessary. 80
- While the particulate dispersed vinyl polymer resin can be and preferably is the same type of polymer i.e., the same polymerized monomer or mixture of monomers, the property requirements of the particulate vinyl polymer resin are distinct and different. Relative to the matrix resin, the particulate dispersed resin must exhibit a higher fluxing temperature, a higher molecular weight, and desirably have an average particle diameter of from 50% to 100% inclusive, of the intended film thickness. 85
- These particulate resins should retain their original form without decomposition at the extrusion temperatures used to produce the film. It is desirable that the fluxing temperature be at least 20° C. and preferably 30° C. greater than the fluxing temperature of the matrix resin. 90
- Preferred vinyl polymer overlay resin compositions are prepared with a vinyl polymer matrix resin exhibiting an inherent viscosity of from 0.60 to 0.82 as measured in accordance with ASTM D-1243 Method A (0.2 gram in 100 milliliters of cyclohexanone at 30° C.) and a vinyl polymer particulate dispersible resin exhibiting an equivalent inherent viscosity of from 0.89 to 1.20 measured as above. Vinyl chloride polymers are especially preferred because of their outstanding properties. 100
- As stated previously the index of refraction of the particulate resin should be similar to that exhibited by the matrix resin if optical quality film is desired. While this is not necessary for pigmented or opaque films, it is critical for optically clear overlay film. It is desirable that the indices of refraction of the two resins be within 0.05. Particles having an index of refraction outside this differential 110
- 120
- 125
- 130

appear as visible specks in the film. Obviously, the dispersible particulate resin must also be compatible with the matrix resin.

The particulate dispersible polymer resin is used in an amount of from 1.0 to 10.0 parts per hundred parts matrix polymer resin and preferably from 1.5 to 5.0 parts per hundred parts matrix polymer resin, all parts by weight. It should be noted that various vinyl polymers normally contain certain additives such as heat and light stabilizers, lubricants, plasticizers, dyes, flexibilizers and the like. Such additives can be present in either or both the matrix vinyl polymer resin and the particulate dispersible vinyl polymer resin as the requirements of such polymer dictate. These resins and their additive requirements as well as the additives themselves are well known in the art and do not warrant additional discussion here.

In the preparation of the compositions and films of this invention the particulate vinyl polymer resin is thoroughly dispersed in the matrix vinyl polymer resin. This is conveniently accomplished by charging the matrix polymer resin and the particulate dispersible resin to a heated ribbon blender or high speed intensive mixer and then to an extruder or other suitable film forming means. The extruder is adjusted to heat the polymer mixture to a temperature in excess of the fluxing point of the matrix resin but below the fluxing point of the dispersed particulate polymer resin. The extruder is fitted with a film producing die and the molten matrix resin containing the dispersed discrete particulate resin is extruded in the form of film.

The extruded vinyl film is characterized by an uneven speckled surface. This film is transparent, when thin, i.e. 1—10 mils but exhibits exceedingly poor optical properties. Refraction appears to be variable. When the film is of greater thickness to 20 mils the surface appears rough and pebbled and the film is translucent rather than clear.

In laminating the vinyl film as an overlay the film and the substrate, preferably vinyl polymer, are placed and held in intimate contact. The lamination is effected and the surface of the overlay is generally planished to an optical quality by pressing the laminate at a pressure of about 300 pounds per square inch between two smooth surfaces,

such as steel plates or rolls, wherein at least that surface contacting the vinyl polymer overlay film is heated to a temperature of above the fluxing temperature of the matrix vinyl polymer but below the melting point of the dispersed particulate resin.

The overlay film of the present invention does not entrap air pockets or blisters during the pressing, lamination or planishing because the irregular surface of the film permits the air to escape. While this problem manifests itself more particularly when using air impermeable substrates such as vinyl polymer plastic sheet it does occur with less frequency when using coated or hard finished paper, cardboard, hardboard, and similar materials. The present invention is applicable to any substrate which can be laminated to or be enveloped by the overlay film. Suitably substrates include paper, cardboard, fiberboard, hardboard, plastic sheet, plastic film, and the like. It is preferred however, when using a vinyl polymer substrate to use an overlay film of the same type of vinyl polymer. For example if the substrate is polyvinyl chloride sheet, it is desirable to use a polyvinyl chloride matrix resin.

While applicant does not intend to be bound by theory it is believed that during the extrusion process of forming the film the discrete particles of unfused resin near the surface cause the surface matrix resin above it to form a bead contour on the surface of the film. This beading results in the rough surface having distorted optical quality. When the film is heat softened and pressed, the beading and the particles at the surface are pressed into the matrix, and flush with the surface resulting in a polished surface which imparts optical characteristics to the film. The dispersed high melting particles having approximately the same refractive index as the matrix resin become invisible and the film appears to be homogeneous.

The example which follows serves to illustrate this invention. Unless otherwise specified all parts and percentages are by weight.

EXAMPLE

A vinyl polymer film forming composition is prepared having the following formulation:

BEST AVAILABLE COPY

4

1,103,212

	Matrix Resin	94.30 per cent
5	Extrusion grade vinyl chloride copolymer resin containing 90 per cent polymerized vinyl chloride and 10 per cent vinyl acetate exhibiting a fluxing temperature of about 180° C., an index of refraction of 1.525 and an equivalent inherent viscosity of about 0.82*	
10	Particulate Dispersible Resin Polyvinyl chloride resin having a fluxing temperature of about 210° C., an index of refraction of 1.54, and an equivalent inherent viscosity of about 1.03*	2.50 per cent
15	Additives Tin Mercaptide Stabilizer Stearic acid Lubricant Blue dye	3.20 per cent 2.50 per cent 0.65 per cent 0.05 per cent Trace

*Determined in accordance with ASTM D-1243 Method A measured at 0.2 gram per 100 milliliters of cyclohexanone at 30° C.

The ingredients are charged to a ribbon blender and are thoroughly admixed. This mixture is charged to a standard heated extruder having a film extruding die fitted to the discharge part of the extruder. The resin mixture is heated to a temperature of 180° to 190° C. and is extruded into a film. This film is characterized by a rough speckled surface. This film is placed over a rigid polyvinyl chloride sheet of the type normally used in the manufacture of identification charge account cards. The two sheets are then placed on smooth heated platens of a press. The films are subjected to a temperature of from 180° C. to 190° C. and a pressure of 300 psi. The overlay sheet is laminated to the substrate sheet and presents a smooth clear surface.

In a similar manner an overlay film is prepared from a polyvinyl chloride matrix resin and a polyvinyl chloride particulate resin.

WHAT WE CLAIM IS:—

1. A thermoplastic composition capable of being extruded as a self-supporting film comprising a low melting thermoplastic vinyl polymer matrix resin as hereinbefore defined and dispersed therein from 1 to 10 per cent by weight of the matrix resin of a particulate high melting vinyl polymer resin having an average particle size of from 20 to 120 microns in diameter, the fluxing temperature of said dispersed particulate resin being at least 20° C. higher than the fluxing temperature of said matrix resin.
2. A composition as claimed in claim 1 wherein the matrix resin is a vinyl chloride polymer.
3. A composition as claimed in claim 1 or claim 2 wherein the thermoplastic vinyl polymer matrix resin exhibits a fluxing temperature of from about 165° C. to about 185° C.
4. A composition as claimed in claim 1 or claim 3 wherein the matrix resin is prepared from styrene, a methoxy-, nitro-, methyl-, or phenyl-derivative of styrene, a vinylidene halide, a vinyl ester, acrylic acid or an alpha-alkyl acrylic acid, an alkyl ester or an amide or a nitrile derived from acrylic acid, an alkyl ester of maleic or fumaric acid, or a vinyl alkyl ether or ketone.
5. A composition as claimed in claim 1 wherein the thermoplastic vinyl polymer matrix resin is substantially as hereinbefore described.
6. A composition as claimed in any one of the preceding claims wherein the matrix resin has an equivalent inherent viscosity of at least 0.1 less than the inherent viscosity of the particulate resin.
7. A composition as claimed in any one of the preceding claims wherein the matrix resin has an inherent viscosity of from 0.60 to 0.82 and the particulate resin has an inherent viscosity of from 0.89 to 1.20.
8. A composition as claimed in any one of the preceding claims wherein the particulate resin is a polymer of the same monomer or mixture of monomers as is the matrix resin.
9. A composition as claimed in any one of the preceding claims wherein the dispersed particulate resin is present in an amount of from 1.5 to 5.0 per cent by weight of the matrix resin.
10. A composition as claimed in any one of the preceding claims wherein the fluxing

- temperature of the dispersed particulate resin is more than 30° C. higher than the matrix resin. 40
11. A composition as claimed in any one of the preceding claims wherein the dispersed particulate polymer exhibits a refractive index value within 0.05 of that exhibited by the matrix resin. 45
12. A composition as claimed in any one of the preceding claims wherein the dispersed particulate resin is a vinyl chloride polymer.
13. A thermoplastic film forming composition substantially as described herein with reference to the Example.
14. A thermoplastic film when prepared from a composition as claimed in any one of the preceding claims.
15. A method of providing a smooth impermeable substrate with a vinyl polymer overlay which method comprises blending a thermoplastic composition comprising a vinyl polymer matrix resin and from 1 to 10 per cent by weight of the matrix resin of a vinyl polymer particulate resin having an average particle size of from 20 to 120 microns in diameter, said particulate resin exhibiting a fluxing temperature of at least 20° C. higher than that exhibited by the matrix resin, heating said resin blend to a temperature above the fluxing temperature of said matrix resin and below the fluxing temperature of said dispersed particulate resin, extruding said resin blend into the form of a film, and thereafter mounting said film on said substrate and laminating said film to said substrate. 50
16. A method as claimed in claim 15 which method further comprises planishing said film by subjecting said film substrate under pressure to a temperature above the fluxing tem- 55
- perature of said matrix polymer and below the fluxing temperature of said particulate resin.
17. A method as claimed in claim 15 or claim 16 wherein the thermoplastic composition is a composition as claimed in any one of claims 1 to 12. 60
18. A method as claimed in any one of claims 15 to 17 wherein the substrate is a vinyl polymer sheet.
19. A method as claimed in any one of claims 15, 16 or 18 wherein the dispersed particulate resin has an average particle size of from 20 to 120 microns.
20. A method as claimed in any one of claims 15, 16, 18 or 19 wherein the vinyl polymer matrix resin is a vinyl chloride polymer. 65
21. A method as claimed in any one of claims 15, 16, 18, 19 or 20 wherein the dispersed particulate vinyl polymer resin is a vinyl chloride polymer resin.
22. A method as claimed in any one of claims 15, 16, 18 or 19, wherein the vinyl polymer matrix resin is a copolymer of vinyl chloride and vinyl acetate.
23. A method of providing a substrate with a vinyl polymer overlay substantially as described herein with reference to the Example. 70
24. Substrates having an overlay provided by a method as claimed in any one of claims 15 to 23.

BOULT WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents,
Agents for the Applicant(s).

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.